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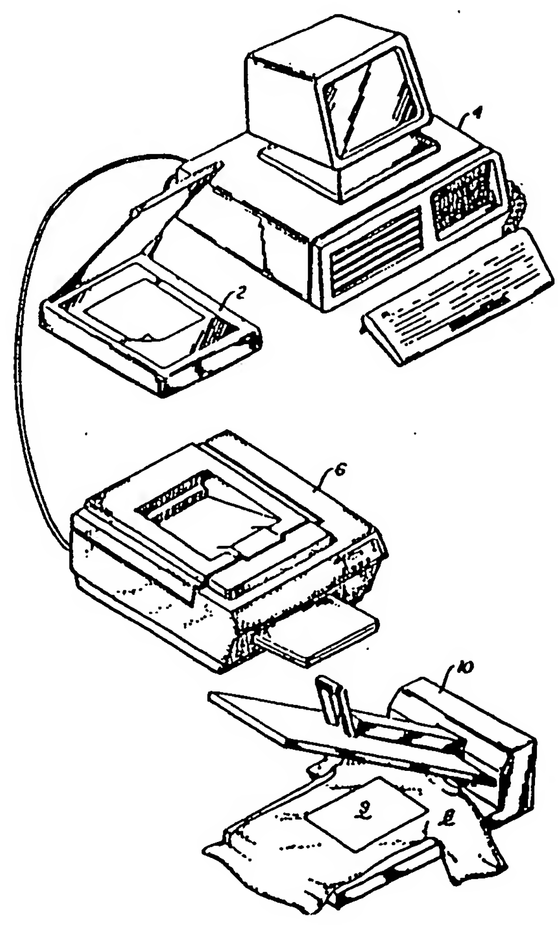
With international search report.
With amended claims.

(54) Title: REACTIVE INK PRINTING PROCESS

(57) Abstract

A method of printing an ink or meltable ink layer which comprises dyes or pigments or other colorants. The ink or ink melt layer comprises compounds with functional groups capable of reacting with active hydrogen, and compounds with functional groups containing active hydrogen, or functional groups capable of conversion to active hydrogen containing groups. An image is printed (6) onto a substrate (9), at a relatively low temperature, so that the ink is not activated during the process of printing (6) on the medium (9). The image is subsequently transferred or permanently fixed on the final substrate (8) by the application of heat and pressure (10), which activates the ink, and bonds the colorant to the final substrate (8). The reactive compounds may be blocked with blocking agents which are removed by the application of heat or other energy during activation of the ink.



To improve the quality of images transferred onto substrates having a cotton component or other absorbent component, substrates are surface coated with materials, such as the coatings described in DeVries et. al., U.S. Patent Number 4,021,591. Application of polymer surface coating materials to the substrate allows the surface coating material to bond the ink layer to the substrate, reducing the absorbency of the ink by the cotton and improving the image quality.

Gross coverage of the substrate with the surface coating material does not match the coating to the image to be printed upon it. The surface coating material is applied to the substrate over the general area to which the image layer formed by the inks is to be applied, such as by spraying the material, or applying the material with heat and pressure from manufactured transfer sheets, which are usually rectangular in shape. To achieve full coverage of the surface coating, the area coated with the surface coating material is larger than the area covered by the ink layer. The surface coating extends from the margins of the image after the image is applied to the substrate, which can be seen with the naked eye. The excess surface coating reduces the aesthetic quality of the printed image on the substrate. Further, the surface coating tends to turn yellow with age, which is undesirable on white and other light colored substrates. Yellowing is accelerated with laundering and other exposure to heat, chemicals or sunlight. A method described in Hale, U.S. Patent No. 5,575,877, involves printing the polymer surface coating material to eliminate the margins experienced when aerosol sprays or similar methods are used for gross application of the polymeric coating material.

Thermal transfer paper can transfer a heat-melt image to a final substrate such as cotton. However, this method has several limitations. First, the entire sheet is transferred, not just the image. Second, such papers are heavily coated with material to bind the heat-melt material on the textile. This material makes the transfer area very stiff. Finally, the laundering durability is not improved to acceptable levels. The thermal transfer paper technology (cited Foto-Wear patent) only creates a temporary bond (heat-melt) between the transfer materials and the final substrate. This bond is not durable to washing.

digital printing of the ink layer can be achieved. The polyols also supply functional groups having active hydrogens which will cross-link with active isocyanate, and permanently bond to the final substrate.

Polyols with a polyether backbone are preferred. In general, polyols or mixtures thereof may have an average molecular weight from 500 to 50,000, and preferably, an average molecular weight in the range of 1,000 to 3,000. The resulting composition, with the rest of the components in the ink layer, is suitable for the digital printing process. The average molecular weight of the whole of all polyol compounds is defined as the sum of the product of the molecular weight and the mole fraction of each polyol compound in the mixture. A preferred embodiment of an ink layer comprises a mixture of high molecular weight polyol compounds having molecular weights of 3000 to 10,000, and low molecular weight polyol compound having molecular weights of not greater than 600.

The polyisocyanate and the polyol compounds are preferred to have an average functionality greater than or equal to two, and not greater than four. The ratio of the equivalents of isocyanate group to the equivalents of hydroxyl group may range from 1/2 to 10/1, preferably 1/1 to 2/1.

Catalysts may be included to speed up the cross-linking reaction. Organometallic compounds are suitable catalysts. Dibutyltin, 0.5% to 4% by weight, based on the isocyanate, may be used.

The colorant may be pigments or dyes. Such colorants comprise from 1% - 20%, and typically 3% - 10%, of the ink, by weight. Suitable dyestuffs include, but are not limited pigments to, Acid Dyes, Basic Dyes, Solvent Dyes and Disperse Dyes. The ink layer may also contain binder material. Generally binders are resins described as non-crystalline solid materials, or liquids of relatively high molecular weight which adhere the colorant to the panel of the ribbon during coating. The following resins and mixtures thereof may be incorporated into the ink panel formulation: Rosin and modified rosins, such as calcium, magnesium, and zinc metallic resinates, ester gum of rosin, maleic resins and esters, dimerized and polymerized rosins and rosin modified fumaric resins; shellac, asphalts, phenolic resins and rosin-modified phenolic resins; alkyd resins; polystyrene resins and copolymers thereof; terpene resins; alkylated urea formaldehyde resins; alkylated melamine formaldehyde resins;

hydrocarbons encapsulated in a microsphere which bursts upon the application of heat. The gaseous products produced upon bursting expand the ink layer.

Simultaneous expanding and crosslinking gives a three dimensional image which is permanently bound to the substrate. The height of the image is dependent on the force of the pressure which is applied during heat transfer printing.

These additives are preferred to be incorporated into a white-colored panel which is positioned adjacent to a dark substrate. The color image so produced is vibrant and visible on the dark fabric.

These additives may be used in the prime layer to assist in the release of the image from the paper.

Any, or all, of the color panels could include foaming agents. The foaming agent is preferred to have a concentration of between 0.1 - 2.0%.

Foaming agents that evolve gas as the result of thermal decomposition are preferably used as the foaming agent. Examples are organic expanding agents such as azo compounds, including azobisisobutyronitrile, azodicarbonamide, and diazoaminobenzene, nitroso compounds such as N,N'-dinitrosopentamethylenetetramine, N,N'-dinitroso-N,N'-dimethylterephthalamide, sulfonyl hydrazides such as benzenesulfonyl hydrazide, p-toluenesulfonyl hydrazide, p-toluenesulfonyl azide, hydrazolcarbonamide, acetone-p-sulfonyl hydrazone; and inorganic expanding agents, such as sodium bicarbonate, ammonium carbonate and ammonium bicarbonate.

Thermally expandable microcapsules are composed of a hydrocarbon, which is volatile at low temperatures, positioned within a wall of thermoplastic resin. Examples of hydrocarbons suitable for practicing the present invention are methyl chloride, methyl bromide, trichloroethane, dichioroethane, n-butane, n-heptane, n-propane, n-hexane, n-pentane, isobutane, isophetane, neopentane, petroleum ether, and aliphatic hydrocarbon containing fluorine such as Freon, or a mixture thereof.

Examples of the materials which are suitable for forming the wall of the thermally expandable microcapsule include polymers of vinylidene chloride, acrylonitrile, styrene, polycarbonate, methyl methacrylate, ethyl acrylate and vinyl acetate, copolymers of these monomers, and mixtures of the polymers of the copolymers. A crosslinking agent may be used as appropriate.

one compound having at least one functional group available for conversion to a group containing active hydrogen, and thereafter, upon the application of sufficient heat, said blocking agent is removed.

10. A method of digital printing as described in claim 8, wherein said at least one compound having at least one functional group which reacts with active hydrogen is an isocyanate.

11. A method of digital printing as described in claim 9, wherein said at least one compound having at least one functional group which reacts with active hydrogen is an isocyanate.

12. A method of digital printing as described in claim 8, wherein said at least one compound having at least one functional group which reacts with active hydrogen is an epoxide.

13. A method of digital printing as described in claim 9, wherein said at least one compound having at least one functional group which reacts with active hydrogen is an epoxide.

14. A method of digital printing, comprising the steps of:

a. preparing an ink comprising a colorant, at least one compound having at least one functional group which reacts with active hydrogen, and at least one compound having at least one functional group containing active hydrogen;

b. supplying a printer with said ink;

c. printing said ink on a first substrate to form an image on said first substrate; and

d. subsequently transferring said image from said first substrate to a

31. A method of digital printing as described in claim 25, wherein said at least one compound having at least one functional group which reacts with active hydrogen is an isocyanate.

32. A method of digital printing as described in claim 26, wherein said at least one compound having at least one functional group which reacts with active hydrogen is an isocyanate.

meltable compound having at least one functional group containing active hydrogen;

subsequently applying heat to said image at a temperature which is above the activation temperature of said thermally removable blocking agent, wherein said thermally removable blocking agent activates and permits reaction of said at least one compound having at least one functional group which reacts with active hydrogen with said at least one heat meltable compound having at least one functional group containing active hydrogen to bond said image to said substrate.

6. A method of digital printing as described in claim 1, 2, 3, or 4, wherein said ink further comprises a blocking agent which, during printing of said ink, prevents a reaction between said at least one compound having at least one functional group which reacts with active hydrogen, and said at least one compound having at least one functional group containing active hydrogen, and thereafter, upon the application of sufficient heat, said blocking agent is removed.

7. A method of digital printing as described in claim 1, 2, 3, 4, 5, or 6, wherein said at least one compound having at least one functional group which reacts with active hydrogen is an isocyanate.

8. A method of digital printing as described in claim 1, 2, 3, 4, 5, 6, or 7 wherein said at least one compound having at least one functional group containing active hydrogen is a polyol.

9. A method of digital printing as described in claim 1, 2, 3, 4, 5, 6, or 8, wherein said at least one compound having at least one functional group which reacts with active hydrogen is an epoxide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/09387

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B32B 3/00, 31/00; B44C 1/165
US CL : 156/230, 234, 235, 237, 239, 240, 241, 247, 277, 289; 428/195
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 156/230, 234, 235, 237, 239, 240, 241, 247, 277, 289; 428/195

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 1.0, APS, STN EXPRESS search terms: carboxylic anhydride, isocyanate, ink jet, print, epoxy, epoxies, epoxide, blocked, polyepoxide, polyisocyanate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,640,180 A (HALE et al) 17 June 1997, see entire document, especially figure 3.	1-32
Y	US 5,607,482 A (REIFF et al) 04 March 1997, see entire document.	1-32
Y	ULRICH, H. Isocyanates, Organic. Ullmann's Encyclopedia of Industrial Chemistry. 1989. Vol A14, 5th ed. pages 611-625.	4, 6-13, 16, 18-19, 23-32
Y	US 5,556,935 A (TRAUBEL et al) 17 September 1996, see entire document, especially abstract.	12-13, 21-22, 27-28
Y	GB 2,036,353 A (JOHANNES) 25 June 1980, see entire document.	12-13, 21-22, 27-28

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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